

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
24 June 2004 (24.06.2004)

PCT

(10) International Publication Number
WO 2004/052116 A1

(51) International Patent Classification⁷: A23D 9/06,
C11B 5/00

(21) International Application Number:
PCT/FI2003/000943

(22) International Filing Date:
10 December 2003 (10.12.2003)

(25) Filing Language: Finnish

(26) Publication Language: English

(30) Priority Data:
20022175 10 December 2002 (10.12.2002) FI

(71) Applicant (for all designated States except US): LAB-
MAX OY (FI/ET); Vesimäentie 2, FIN-15870 Hollola (FI).

(72) Inventor; and

(75) Inventor/Applicant (for US only): REPO, Harri (FI/ET);
Rautatiekatu 14 B 12, FIN-15110 Lahti (FI).

(74) Agent: TAMPEREEN PATENTTITOIMISTO OY;
Herväankatu 12 B, FIN-33720 Tampere (FI).

(81) Designated States (national): AE, AG, AL, AM, AT (uti-
lity model), AU, AZ, BA, BB, BG, BR, BY, BZ, CA,

CH, CN, CO, CR, CU, CZ (utility model), CZ, DE (uti-
lity model), DE, DK (utility model), DK, DM, DZ, EC, EE
(utility model), EE, EG, ES, FI (utility model), FI, GB, GD,
GH, GI, GM, GR, GU, ID, IL, IN, IS, JP, KE, KG, KP, KR,
KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN,
MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT (utility
model), PT, RO, RU, SC, SD, SE, SG, SK (utility model),
SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,
VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (BW, GH,
GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HU, IL, IT, LU, MC, NL, PT, RO, SE,
SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA,
GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: FOOD OIL PRODUCT AND THE USE OF THE SAME

(57) Abstract: The food oil product is based on turnip rapeseed oil or rapeseed oil. The oil contains tocopherol antioxidant and
α-lipoic acid as regenerator for the antioxidant.

WO 2004/052116 A1

WO 2004/052116

1

Food oil product and the use of the same

The invention relates to a food oil product, which is based on turnip rapeseed oil or rapeseed oil and contains antioxidant. The invention
5 relates especially to a turnip rapeseed -based or rapeseed-based food oil product replacing butter, margarine and flour treatment agents in baking and food processing. The invention also relates to the use of a food oil product.

10 Hardened turnip rapeseed oil or rapeseed oil is the healthiest vegetable fat alternative. On the basis of its composition, this vegetable oil is better than, for example, olive oil.

The problem of oil is becoming rancid, which also damages the food
15 product containing it. Rancidity affects especially the odour and taste of the product and thus directly consumer satisfaction. This problem occurs, for example, when preserving a product for a long time. Becoming rancid is, in addition, faster if the product is kept at room temperature. There are several turnip rapeseed oil -based or rapeseed
20 oil -based food product oils on the market, where efforts to improve rancidity prevention have been made with antioxidants.

Rancidity in food oil is a complex process, which produces reactive
25 units, such as organic peroxides, alcohols, aldehydes, ketone compounds, and carbonylic acids. Of the many possible oxidation reactions, the most common is the formation of free radicals in the fatty acids containing a double bond, which are otherwise recommended in a diet. These free radicals bind oxygen and form a peroxide radical, which enables a chain reaction and produces organic peroxides as a
30 main product. These peroxides transform into secondary products, such as alcohol and carbonyl compounds, which further oxidize into carboxylic acids. At the same time the tocopherols contained in the turnip rapeseed oil lose their antioxidant properties. Rancidity may take place in storage conditions, but especially the fats in food oil are
35 exposed to becoming rancid in connection with use and when the oil is in a finished food product, because these situations involve a high temperature and a oxygenous environment. Thus, the quality of the

WO 2004/052116

PCT/FL2003/000943

2

food oil has a crucial effect on the quality of the food product manufactured by means of it, especially pastries.

5 The existing known product solutions use propyl gallate, butyl hydroxy anisole (BHA), butyl hydroxy toluene (BHT), or ascorbic acid or some of their compounds as antioxidants. Lecithin emulgator is generally used as emulgators. Mixtures formed in different hardened fats, part of which include enzymes, are used as flour enhancers.

10 Synthetic antioxidants, such as butyl hydroxyl anisole (BHA) and butyl hydroxy toluene (BHT), may cause unwanted side effects if their recommended daily dosage is exceeded. Indeed, this has caused an even growing interest in natural antioxidants.

15 The purpose of the invention is to remove the problems connected to especially the preservability of a product and a food product manufactured by means of the product, and to provide a food oil product containing double bond fatty acids, which remains unrancid significantly longer than the present products, and which is based on
20 natural antioxidants. The natural antioxidants here refer to antioxidants, which can be found in nature but which can either originate in natural materials or be manufactured synthetically.

25 A purpose of the invention is also to provide a multifunctional pumpable and unhardened unrancid turnip rapeseed oil -based or rapeseed oil -based food oil containing unsaturated fats (triglycerides), which can be used in food product manufacture as the oil remaining in the food product, especially in baking as the baking oil.

30 To attain this purpose, the product according to the invention is primarily characterized in that it contains α -lipoic acid as regenerator for the antioxidant. The alpha-lipoic acid is significant especially from the point of view of the preservability of a product manufactured by means of the food oil, because it retains the effect of tocopherol
35 antioxidants and prevents rancidity for a long time in a finished product.

WO 2004/052116

PCT/FI2003/000943

3

With a system of additives according to an advantageous embodiment, it is possible to create the first pumpable, unhardened fat containing vegetable oil product, which comprises turnip rapeseed oil and/or rapeseed oil as a base, as well as tocopherol as antioxidant, lecithin (E322) as emulgator, mono and diglycerides of fatty acids (E471), acetic acid esters of the mono and diglycerides of fatty acids (E472a) or sucrose esters of fatty acids (E473); for acidity regulation it is possible to use citric acid (E330); alpha-lipoic acid is used as the regenerator for the tocopherol mixture (E306) used as antioxidant, enzymes capable of splitting the organic long chain components of the raw material of the food product (flour in the case of baking) are used as enzymes, such as amylase and/or pentosanase and possibly hemicellulose, which can be, for example *Aspergillus niger*, *Trichoderma longibrachiatum* and *Aspergillus oryzae* -based enzymes, in order to bring about the lightness of the structure of a bakery good and to improve durability of sub-zero storage. With said enzyme addition, it is possible to replace the separately added enzyme-containing flour enhancers, and thus the product is especially suitable for yeast doughs (doughs raised with yeast) and frozen doughs. Aromas, if they are used, are selected according to necessity from the group of fat-soluble aromas. It is possible to use, for example, butter aroma.

With a suitable system of additives it is thus possible to improve the multifunctionality. When one or more enzymes are used, a pumpable and unhardened unrancid turnip rapeseed oil -based or rapeseed oil -based baking oil containing non-saturated fats (triglycerides) is provided, which at the same time acts as flour enhancer thus replacing the conventional flour enhancers added as powders or as other separate dosage. This type of baking oil containing one or more enzymes is also suitable for manufacturing frozen doughs. When butter aroma is used in the product, in addition to the above, a baking oil is provided, which at the same time provides a butter aroma to the finished baked product. It is also possible to use some other fat-soluble aroma, if some other specific aroma is wanted for the finished product. Butter aroma or some other fat-soluble aroma can also be used without enzymes.

WO 2004/052116

PCT/FL2003/000943

4

In the following, the invention will be described more in detail by means of some examples, which do not restrict the invention.

- 5 All the products were made in a turnip rapeseed base. The main raw material of the oil was turnip rapeseed oil pressed out without chemicals by Mildola Oy. The natural tocopherol level of oil was approx. 25 mg/kg. Examples of the products are presented in the following table (amounts as percentages of weight).

10

	1	2	3	4	5	6	7
Raffinated turnip rapeseed oil or rapeseed oil	98,613	99,288	98,788	98,719	96,839	96,539	96,439
Lecithin soy/turnip rape	1,325	0,650	-	-	-	-	-
E 473	-	-	1,150	-	-	-	-
E 472a	-	-	-	0,200	0,150	0,180	0,180
E 472e	-	-	-	1,000	1,000	2,000	2,000
Alpha-tocopherol	0,002	0,002	0,002	0,003	0,003	0,003	0,003
Gamma-tocopherol	0,015	0,015	0,015	0,023	0,023	0,023	0,023
Delta-tocopherol	0,010	0,010	0,010	0,015	0,015	0,015	0,015
Citric acid	0,020	0,020	0,020	0,020	0,020	0,020	0,020
Alpha-lipoic acid	0,015	0,015	0,015	0,020	0,020	0,020	0,020
Pentosanase/alpha-amylase enzyme	-	-	-	-	1,045	1,045	1,045
Hemicellulose/amylase enzyme	-	-	-	-	0,885	-	-
Alpha-amylase enzyme	-	-	-	-	-	0,155	0,155
Butter aroma	-	-	-	-	-	-	0,100

- 15 In product 1, soybean lecithin is used as an emulgator and in product 2 turnip rapeseed lecithin. In product 3, the emulgator is sucrose esters of fatty acids (E473). In products 4 to 7, the emulgator is a mixture of acetic acid esters and the mono and diacetyl tartaric acid esters of mono and diglycerides of fatty acids (E472a + E472e), in products 5 to 7 alpha-amylase and pentosanase are used as enzyme additions, and in product 5 in addition to these also hemicellulose/amylase enzyme
- 20 Nutrilife CS 16, hemicellulose/amylase: Nutrilife k-FQ10, alpha-amylase: Nutrilife AM17, all produced by

WO 2004/052116

PCT/FI2003/000943

5

Grünau Illerliseen GmbH), and in product 7, butter aroma is used. All products are provided with a mixture of alpha, gamma and delta-tocopherol as antioxidant (more in products 4 to 7) and alpha-lipoic acid as the regenerator of tocopherol antioxidant (more in products 4 to 7). All products are also provided with citric acid (E330) as pH controller and catcher of metal ions. The amount of tocopherols is stated as the tocopherol added to the product in the table, and it is to be noted that in addition to these, it also includes natural tocopherol from the turnip rapeseed oil base. The added tocopherol mixture contains typically 5 to 10 weight-% of alpha-tocopherol, 40 to 65 weight-% of gamma-tocopherol and 25 to 55 weight-% of delta-tocopherol. This type of a tocopherol mixture is added advantageously so much, that the total tocopherol of the product (including the inherent one in the oil) is at least 0.02 weight-%.

15

The added synthetic tocopherol is sensitive and acts as a fast antioxidant. It is advantageous that the added synthetic tocopherol is a mixture of at least gamma and delta-tocopherol.

20

In addition, the sucrose esters of fatty acids have the effect that they create a brown colour when heated, which can be desirable in baking, because in this way the brown/brownish colour on the surface of pastries can be provided without sugar addition.

25

The enzymes are well protected in the oil, and they begin to act in the food product environment when they come into contact with the components contained in the flour. Therefore, flour enhancers are not necessary to be added separately in baking. When the product containing enzymes is used in manufacturing frozen dough, it can compensate for the decrease in the activity of the yeast contained in the dough during freezing.

30

The effect of antioxidants can still be increased by means of ascorbic acid. If the product is provided with ascorbic acid, it improves the effect of alpha-lipoic acid in water environment, i.e. it prevents the food oil from becoming rancid in a food product containing water. Thus, the effect of the ascorbic acid begins when the food oil comes into contact

35

WO 2004/052116

PCT/FI2003/000943

6

with the water contained in the raw material of the food product, for example when adding food oil into a dough during baking. Thus, it is possible to prevent the rancidity of the actual food product with ascorbic acid.

5

The ascorbic acid is advantageously added when dissolved in a carrier substance, which, being fat-soluble, can distribute the ascorbic acid homogeneously into the food oil product. Thus, it is possible to use the natural water-soluble ascorbic acid without resorting to fat-soluble ascorbic acid derivates. The carrier substance is short chain alcohol, advantageously propylene glycol or ethanol. More advantageously the substance is propylene glycol (propane-1,2-diole), which is approved in the EU as a carrier substance used in food products (E code E1520), and which has a high flash point. The carrier substance, where the ascorbic acid is in a concentration of 15 to 30 weight-%, can be added to the food oil product by the amount that corresponds to the desired concentration of the ascorbic acid in the oil product. The concentration can be, for example, 0.02 to 0.2 weight-%, advantageously 0.05 to 0.1 weight-% of the product weight. The fat-soluble antioxidant provided in this way acts already in the oil phase advantageously by significantly decreasing the rancidity tendency of the food oil product containing non-saturated fats. The use of ascorbic acid in vegetable oils, such as turnip rapeseed oil, is described more in detail in the inventor's Finnish patent application 20031190, which is incorporated herein by reference.

25

If the emulgator is turnip rapeseed lecithin, it is possible to increase the antioxidant effect of tocopherols further with it. In addition, turnip rape lecithin is allergy-free. The added lecithin is advantageously hydrolysed lecithin. The turnip rapeseed oil contains inherent lecithin as well, and with the addition, the lecithin content is increased to the desired level.

30

The task of the turnip rapeseed or rapeseed oil component is to function as the carrier substance of all other components, and it is composed in a known manner mainly of triglycerides of long chain fatty acids, and it contains triglycerides of non-saturated fatty acids. The amount of oil component is generally at least 95 weight-%.

35

WO 2004/052116

PCT/FI2003/000943

7

The product 2 of the above-mentioned table and known food oil products were tested in the tests.

- 5 Testing the oil samples was performed with the Rancimat 743 device, which is manufactured by Metrohm Ltd., Switzerland. The method used is generally called the "Rancimat method" (*Laubli, M.W. and Bruttel, P.A. Determination of the oxidative stability of fats and oils; comparison between the active oxygen method (AOCS Cd 12-57) and the rancimat method. J. Am. Oil Chem. Soc. 63: 792-795 (1986)).*
- 10

In the test, 6 grams of the samples were weighed to the reaction vessel, and the samples were heated to 120 °C. A continuous air flow at a rate of 20 l/h was directed to the samples. Electroconductivity was measured from the test vessels, into which 60 mL of distilled water has been dosed.

15

Of the results it can be stated that with the above-mentioned antioxidant packet a result 61.7 h was received in the Rancimat test, which is almost on the same range as the hydrogenated (not containing double bonds) turnip rapeseed oil raffinates (Akorex, Karlshamn). On the other hand, when performing the same tests on known turnip rapeseed oil products containing antioxidants, values of 1.0 to 18.2 h were received. When the concentration of the antioxidant packet (tocopherols and alpha-lipoic acid) was reduced to a half of the above-described concentration in product 2, a value of 56.6 h was still reached.

20

25

The effect of alpha-lipoic acid best becomes apparent by comparison with a product where 0.024 weight-% of synthetic tocopherol mixture without alpha-lipoic acid is added to the turnip rapeseed base: the value was only 17.0 h, even though the amount of tocopherol was on the same level.

30

35 The products according to the invention can be used as liquid, pumpable baking oils replacing baking margarines and butter. The baking oil can be used in a dough in an amount of 1 to 15 weight-% of

WO 2004/052116

PCT/FI2003/000943

8

the fresh weight of the dough. When a product containing enzymes is used as baking oil and it is used to make frozen dough, its amount is 0.5 to 2.0 weight-%, typically approximately 1.0 weight-% of the fresh weight of the dough.

5

The oil according to the invention is especially suitable to be added as baking oil to yeast doughs when baking rolls, buns and breads, but the invention is not limited to these.

10

In addition, the invention is not limited to only baking, but it can be used in manufacturing other food products as well, especially in situations where the oil comes into contact with water in the food product and heating is involved in the manufacturing process.

WO 2004/052116

PCT/FI2003/000943

9

Claims:

1. A food oil product, which is based on turnip rapeseed oil or rapeseed oil and contains tocopherol antioxidant, **characterized** in that it contains α -lipoic acid as regenerator for the antioxidant.
2. The product according to claim 1, **characterized** in that the tocopherol antioxidant contains added synthetic tocopherol.
3. The product according to claim 2, **characterized** in that the tocopherol contains at least gamma and delta tocopherol.
4. The product according to any of the preceding claims, **characterized** in that there is at least 0.02 weight-% of tocopherol and at least 0.002 weight-% of alpha-lipoic acid.
5. The product according to any of the preceding claims, **characterized** in that it contains turnip rapeseed lecithin.
6. The product according to any of the preceding claims, **characterized** in that it contains ascorbic acid.
7. The product according to any of the preceding claims, **characterized** in that it contains enzyme, such as amylase, pentosanase and/or hemicellulase.
8. The use of a product according to any of the preceding claims in manufacturing a food product, especially in baking.
9. The use of a product according to any of the preceding claims in manufacturing a food product in such a manner that it becomes in contact with the water contained in the food product during heating, especially in baking.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 2003/000943

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: A23D 9/06, C11B 5/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: A23D, C11B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL, WPI DATA, PAJ, FROSTI, FSTA, BIOSIS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Z Lebensm Unters Forsch A, Vol. 208, 1999, Heike Drinda et al, "ANTIOXIDANT PROPERTIES OF LIPOIC AND DIHYDROLIPOIC ACID IN VEGETABLE OILS AND LARD", page 270-271, 275	1-9
Y	Eur. J. Lipid Sci. Technol. Vol. 103, 2001, Nedyalka V. Yanishlieva et al, "STABILISATION OF EDIBLE OILS WITH NATURAL ANTIOXIDANTS", page 752-753, 757.	1-9

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

6 April 2004

Date of mailing of the international search report

15-04-2004

Name and mailing address of the ISA/
Swedish Patent Office
Box 5055, S-102 42 STOCKHOLM
Facsimile No. +46 8 666 02 86

Authorized officer

Johanna Brolund/MP
Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 2003/000943

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Week 199321 Derwent Publications Ltd., London, GB; Class B05, AN 1993-174387 & SU 1738285 A1, (NON-BLACK SOIL AREA VETERINARY INST), 07 June 1992 (1992-06-07) abstract</p> <p>--</p>	1-9
A	<p>Plant Physiol. Biochem. Vol. 40, 2002, Flavia Navari-Izzo et al, "Lipoic acid: a unique antioxidant in the detoxification of activated oxygen species" page 464, column 1; page 466, column 2; page 467; abstract</p> <p>--</p>	1
A	<p>US 5260077 A (VIRGINIA A. CARRICK ET AL), 9 November 1993 (09.11.1993), column 1 - column 2; column 3, line 1 - line 9; column 4, line 66 - line 68, claims 1,10,28</p> <p>--</p>	1-9
A	<p>EP 326829 A2 (SOCIETE DES PRODUITS NESTLE S.A.), 9 August 1989 (09.08.1989), page 2 - page 3, claims 1-3,7</p> <p>--</p>	1-9
A	<p>BIOCHEMICAL AND BIOPHYSICAL RESEARCH COMMUNICATIONS, Vol.204, No. 1. 1994, M Podda et al. "a-LIPOIC ACID SUPPLEMENTATION PREVENTS SYMPTOMS OF VITAMIN E DEFICIENCY",page 98-99; abstract</p> <p>-- -----</p>	1-9

INTERNATIONAL SEARCH REPORT

Information on patent family members

27/02/2004

International application No.

PCT/FI 2003/000943

US	5260077	A	09/11/1993	MX	9200592	A	01/08/1992
EP	326829	A2	09/08/1989	NONE			